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Aluminum as energy carrier: Feasibility analysis and current technologies overview

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ABSTRACT

Aluminum is examined as energy storage and carrier. To provide the correct feasibility study the work includes the analysis of aluminum production process: from ore to metal. During this analysis the material and energy balances are considered. Total efficiency of aluminum-based energy storage is evaluated.

Aluminum based energy generation technologies are reviewed. Technologies are categorized by aluminum oxidation method. Particularly, the work focuses on direct electrochemical (anodic) oxidation of aluminum, aluminum–water reaction in alkaline solution, mechanochemical activation of aluminum, mechanical activation of aluminum and high-temperature aluminum–water reaction. The objective is methods overview including technological principle, efficiency, urgent problems and possible application areas.

Contents

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1. Looking for an appropriate energy carrier

1.1. Need for energy storage technologies

A number of independent institutions predict that the oil, today's basic fuel in transport and small stationary energy, in near future will peak and its production will go into decline [1–6]. One of the world energy scenarios supposes that oil production would not exceed 90 million barrel/day and decline will start before 2020 [7]. Oil production reduction is going to be provided not only by oil reserves depletion but also due to efforts in alternative energy. It is predicted that renewable-based electricity generation will triple between 2008 and 2035 and increase in global generation from 19% in 2008 to almost one-third in 2035 [7]. At the same time the backbone of global energy in the next decades will remain the coal and word's base electricity load will be attached to large and remote coal-fired units. To remove the oil from transport, to support the renewable, distributed and Smart-grid energy and to smooth the load of centralized coal-fired and nuclear power plants, the energy storage technologies are required. To sum up, oil problems, efforts in renewables and coal predominance, as well as continued human industrialization and informatization all together need to store the energy.

Energy storages are urgently needed at all energy scales: from portable and transport to large stationary. Different applications can make significantly various demands, thus diversifying the spectrum of energy storage technologies. Today the variety of energy storage includes the following: batteries (lead-acid [8–11], sodium sulphur [12], Ni-based [13,14], Li-based [15–18], flow batteries [19–21], etc.), supercapacitors [22], superconducting magnetic energy storage [23], flywheel storage [24,25], pumped hydro storage [26], pneumatic storage [27–29] and others. Energy storage technologies have been already reviewed and compared [30–37]. The summary of recent reviews is presented in Table 1. Although there are a great number of commercially available energy storage technologies, none of above listed systems can be referred to as universal and each has its own specialized application areas. Sodium sulphur battery, vanadium redox flow battery, pumped hydro storage and compressed air energy storage are only stationary. Most technologies return the energy back to the grid. Only conventional batteries such as lead-acid, nickel cadmium and lithium ion are supposed to carry the energy. Batteries have high electrical efficiency, rapid response and relatively low self-discharge, but suffer from low energy density and short lifetime. Last disadvantages prevent the batteries from large-scale (over 50 MWh per unit) energy storage applications. Moreover, if the capacity of conventional batteries increases, there will be a problem of the natural abundance of used metals [33,38]. Therefore, there are still no sustainable alternatives for energy carrying and the replacement of oil from its traditional niches by energy storage technologies seems to be far from reality.

1.2. Perspective inorganic energy carriers

High-level integration like with liquid hydrocarbons within global energy is possible only in case of energy carriers based on the most widespread chemical elements in the earth's crust or lithosphere. In simple case the energy can be stored in the form of chemical energy of reduced inorganic substances such as hydrogen [39,40], silicon [41], aluminum [42], iron [43], magnesium [44] and others. The process of energy accumulation occurs when the substance is produced from respective oxide. The energy is then regenerated, when the substance is oxidized. Such energy carriers differ from the conventional energy storage technologies because they represent the renewable synthetic fuels. They can be stored for a long time with negligible self-discharge and easily transported to any distance like fossil fuels.

Hydrogen has been already recognized to be one of perspective future energy carries. It can be produced from water through electrolysis that means that the potential reserve of hydrogen on the Earth is practically unlimited. Hydrogen is proposed to be used as a fuel in portable [45] and transport [46] and as energy storage in renewable and conventional power plants [30,32,33]. Especially, hydrogen production is bound up with nuclear reactors because of benefits of high temperature electrolysis [47–50]. Although hydrogen-based energy storage system has relatively low cycle efficiency, about 35% [32] (due to the combination of electrolytic cell and combustion cell), the hydrogen is much attractive energy carrier, because, theoretically, it has high energy density, can be used to store large amounts of energy and can be transported for a long distance (to remote non-electrified areas). Moreover, hydrogen is environmentally friendly in terms of that the process of its combustion is less polluting than that of fossil fuels, so the use of hydrogen for energy production decreases the charges for eco-activity. However, in spite of the fact that hydrogen energy has been under research for several decades up to now and for this time it has changed into individual scientific area [51], the hydrogen still has not obtained the recognition of energy market mainly due to storage and transportation problems [46,52], which are still open as decades ago.

While hydrogen is stopping, the attention falls on other energy carriers. To compete with hydrogen and oil in basic fields the alternative inorganic energy carrier must first of all be composed of the most widespread substances like those presented in Table 2. The use of presented substances in synthetic fuel production should expand the spectrum of suitable minerals and so decrease the fuel cost. There is a dream to use ordinary sand as raw for synthetic fuel [41,53]. However, an appropriate fuel composition must be formed in accordance with both production process and oxidation technology efficiencies. Generally speaking, there is a wide spectrum of differently composed inorganic synthetic fuels, which might be used for energy storage and carrying, especially in post-fossil fuel era; the time will show which one will get the sustainability.

1.3. Reasons for aluminum

Present work will be focused on aluminum. Unlike hydrogen, aluminum is easy to transport and store. When metal is placed into the atmosphere, it is covered by oxide film, which protects metal from further corrosion [54], thus providing the safety of its storage and transportation. Like hydrogen, aluminum is renewable. It has high calorific value, high concentration in the earth's crust [55,56] and high current production level [57–59]. So, aluminum can be regarded as perspective energy carrier and has a good chance for large-scale integration in global energy storage.

To provide the correct feasibility study this work will be started from aluminum production process analysis, which will examine the whole chain: from ore to metal. During this analysis the material and energy balance will be considered.

Then, the technologies, which use aluminum as fuel or energy source, will be reviewed. Technologies differ from each other manly by aluminum oxidation method. When aluminum is oxidized the oxide film, which provides the safety of aluminum storage and transportation, creates an obstacle to efficient utilization of aluminum within power plants. To increase the efficiency of aluminum-based energy generation technology the special actions such as alloying with certain elements, chemical activators addition, mechanical or mechanochemical treatment, heating and other are applied. The objective of this work is such methods overview including technological principle, efficiency, urgent problems and possible application areas.

Table 1
Comparison of energy storage technologies.

Energy storage technology	Capacity range	Typical self-discharge	Cycle efficiency, %	Energy density, Wh/kg	Power density, W/kg	Lifetime	Application areas
Lead-acid battery	1 W–10 MW	2%/month	70–90	30–50	100–200	1200–1800 cycles	Portable, electric/hybrid electric vehicle, small stationary
Nickel cadmium battery	1 W–40 MW	10%/month	60–83	50–75	150–300	1500–3000 cycles	Portable, small stationary
Nickel metal hydride battery	1 W–100 kW	30%/month	65–70	50–80	200–600	1500–3000 cycles	Portable, electric/hybrid electric vehicle
Sodium nickel chloride	1 W–300 kW	15%/day	70–80	100–120	150–200	2500 cycles	Portable, hybrid electric vehicle
Sodium sulphur battery	50 kW–34 MW	20%/day	75–92	150–240	150–230	2500–4500 cycles	Large stationary, power quality
Lithium ion battery	1 W–100 kW	5%/month	85–100	100–200	150–300	1000–10,000 cycles	Portable, electric/hybrid electric vehicle, small stationary
Lithium polymer battery	1 W–100 kW	5%/month	85–100	150	150–250	300–600 cycles	Portable, electric/hybrid electric vehicle, small stationary
Vanadium redox flow battery	50 kW–250 kW	Small	75–85	10–30		>13,000 cycles	Small stationary
Supercapacitor	1 W–300 kW	5%/day	85–98	0.5–5	>10,000	>500,000 cycles	Portable, hybrid electric vehicle, power quality
Superconducting magnetic energy storage	1 MW–100 MW	10%/day	97–100	0.5–5	500–2000	>100,000 cycles	Power quality
Flywheel storage	100 kW–250 kW	20%/h	90–95	5–100	>1000	20 years	Small stationary, power quality
Pumped hydro storage	1 MW–5000 MW	Small	70–85	0.5–1.5		60 years	Large stationary
Compressed air energy storage	50 MW–300 MW	Small	50–89	30–60		40 years	Large stationary

Table 2
Characteristics of energy storage matters.

Substance	Content in lithosphere, wt.%	Density, g/cm^3	Calorific value, MJ/kg	Heat generation in water oxidation reaction, MJ/kg	Mass of H_2 produced in water oxidation reaction per a kg of substance, kg
Si	27.72	2.42	30.74	10.24	0.143
Al	8.13	2.7	30.97	15.03	0.111
Fe	5	7.87	7.35	−0.33	0.054
Ca	3.63	1.55	15.91	8.74	0.050
Na	2.83	1	9.05	2.82	0.043
Mg	2.09	1.74	25.11	13.16	0.083

2. Aluminum production process analysis

2.1. Geology

Aluminum is one of the most widespread chemical elements in the outer 16 km of the crust (about 8% by weight [60,61]); only oxygen and silicon are more widespread, while among metals aluminum takes first place. The earth's crust contains aluminum mainly in the form of aluminum silicates.

The main raw for aluminum production is crystalline aluminum oxide – alumina (Al_2O_3). Although alumina is contained within a great number of natural minerals, about 98% of metallurgical alumina is produced only from bauxite. Bauxite is a compound rock, which is composed of hydrous alumina (aluminum hydroxides and oxyhydroxides). There are also various compounds in bauxite such as iron oxide, silicon oxide, titanium dioxide and smaller amounts of other oxides. Bauxite contains 50–80% of hydrous alumina. The percentage of alumina varies from 30% to 60%. The composition of bauxite mined differs depending on mining location [62–66]. Table 3 shows bauxite composition suitable for metallurgical alumina production. Bauxite resources are estimated to be 55–75 billion tons [56] that is 275–375 times more than current annual rate of its extraction (about 200 million tons [56,67]).

2.2. Alumina refining

Of all bauxite mined, approximately 85% is used for metallurgical alumina production [68]. Alumina is extracted from bauxite by

Table 3
Composition of bauxite suited for metallurgical alumina production.

Compound	Content, wt.%
Al_2O_3, min	30
SiO_2, max	20
Fe_2O_3, max	30
TiO_2, max	6
other, max	1

Table 4
Components of alumina prime cost.

Item	%
Total	100
Bauxite	24
Auxiliary raw	9
Energy	24
Investment	26
Wage cost & repair bill	17

Bayer process. The chemistry of this process can be simplified by the following equation:

$$Al_2O_3{\cdot}nH_2O + 2NaOH \rightleftarrows 2NaAlO_2 + (n+1)H_2O \quad (1)$$

Bayer process is usually considered in four stages [69]. The first is the digestion. Bauxite is heated together with aqueous solution of sodium hydroxide within special digesters where hydrous alumina dissolves to form sodium aluminate solution – equilibrium of reaction (1) shifts to the right. Digester temperature is set from the interval of 140–240 °C depending on bauxite composition. During the second stage known as clarification, the resulting liquor is purified from red mud (insoluble residue). The mud is then thickened and washed to recover the alkali, which is sent back to the digestion process. The third stage is precipitation, in which aluminum hydroxide at temperatures about 45–70 °C is precipitated – equilibrium of reaction (1) shifts to the left. And finally, aluminum hydroxide is calcined at temperatures about 1150–1300 °C to produce alumina during the so-called calcination stage.

Prime cost of alumina is assembled from bauxite cost, auxiliary raw (alkali, limestone and other) cost, energy (thermal and electrical) cost, investment cost, wage cost and repair bill. Approximate cost distribution for alumina is shown in Table 4 [70]. Energy intensity of alumina is estimated to range from 7 to 35 MJ/t [69–72] depending on bauxite quality and alumina refining technology.

2.3. Aluminum smelting

Such standard methods of metal production as carbon reduction or electrolysis from aqueous solution are unsuitable for aluminum. Carbon reacts with aluminum producing aluminum carbide; in the process of electrolysis within aqueous solutions the hydrogen is reduced on the cathode instead of aluminum because aluminum is more electronegative.

For aluminum electrolysis the cryolite (Na_3AlF_6) was established to be the best electrolyte. Cryolite does not contain metals, which can be precipitated on the cathode instead of aluminum. It has a density less than that of aluminum at operating temperatures: at 950–1000 °C the density of cryolite is less than 2.1 g/cm^3, while aluminum density at these temperatures is about 2.3 g/cm^3 [73] that positively influences on aluminum sedimentation within the electrolyzer.

Theoretically, cryolite isn't consumed during the electrolysis. However, practically, at least 20 kg of cryolite materials (Na_3AlF_6, AlF_3, NaF) per a kg of aluminum are added into electrolysis bath [69]. Cryolite is not so abundant and for industrial purposes it is produced from fluorspar (CaF_2).

Molten cryolite dissociates into ions in the following way:

$$Na_3AlF_6 \rightarrow 3Na^+ + AlF_6{}^{3-},$$

Alumina dissociation can be described by the following equation:

$$Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}.$$

Al^{3+} and Na^+ ions are moved to the cathode, but mainly aluminum ions are discharged because they are more electropositive:

$$Al^{3+} + 3e^- \rightarrow Al,$$

$AlF_6{}^{3-}$ and O^{2-} are moved to the anode, where oxygen ions are discharged:

$$2O^{2-} - 4e^- \rightarrow O_2.$$

Overall process of aluminum electrolysis is described by the following equation:

$$Al_2O_3 \rightarrow 2Al + 1.5O_2. \quad (2)$$

Eq. (2) corresponds to electrolysis, in which the anode is non-consumable – inert (based on platinum, ferrite, nitride or other). However, industrial process, the Hall-Héroult process, is based on carbon anodes. Electrolyzers based on inert anode still represent the field of research and development [74–81].

Hall-Héroult process can be described by the following equation:

$$Al_2O_3 + nC \rightarrow 2Al + (3-n)CO_2 + (2n-3)CO. \quad (3)$$

Industrial anodes are composed of calcined coke (70–80 wt.%) and pitch (14–35 wt.%) as a binder [73]. Two different anode types are currently used: self-baking and prebaked. Anode consumption rate ranges from 0.4 to 0.5 kg of carbon per a kg of aluminum depending on anode type and electrolysis conditions [73]. Resulting anodic gas is composed of 30–50% CO and 50–70% CO_2. About 8 kg of CO_2-equivalent (including emissions from power plants) per a kg of aluminum are released when aluminum is electrolytically produced [82–84].

The use of inert anodes is intended to make the aluminum production more environmentally friendly. However, smelting based on inert anode requires more electrical energy than carbon-based smelting: theoretically, the minimum energy requirement for process (2) is 51% higher than the process (3) requirement [69].

The necessary charge is defined from Faraday's law:

$$q = \frac{A}{z \times F}, \quad (4)$$

where q – electrochemical equivalent, A – atomic mass, Z – valency, F – Faraday's constant. In case of aluminum Eq. (4) gives the following:

$$q = \frac{26.98154}{3 \times 96485.309} = 9.3215 \times 10^{-5}\ \frac{g}{A \times s},$$

i.e., theoretically, 1 Ah should produce 0.335 g of aluminum. But, practically, the mass of aluminum produced is less then theoretical value. Electrolyzers with self-baking anodes have 88% current efficiency, electrolyzers based on prebaked anodes reach 91–94% current efficiency [85]. Electrical energy intensity of aluminum varies from 13.4 kWh/kg for state-of-the-art electrolyzing technologies up to more than 20 kWh/kg for older plants [69].

2.4. Material and energy balance

Material balance for primary aluminum production process is schematically shown in Fig. 1. 4 kg of bauxite give about 2 kg of alumina, which then give about 1 kg of aluminum.

The energy required to raw materials preparing and aluminum smelting was estimated to be 85.6 MJ/kg of aluminum [69]. It is summed of 56 MJ of electrical energy and 29.6 MJ required for raw materials. Raw materials energy is composed of 1.1 MJ for bauxite mining, 26.1 MJ for alumina refining and 2.4 MJ for carbon anode production. Since the heat content of carbon required per a kg of

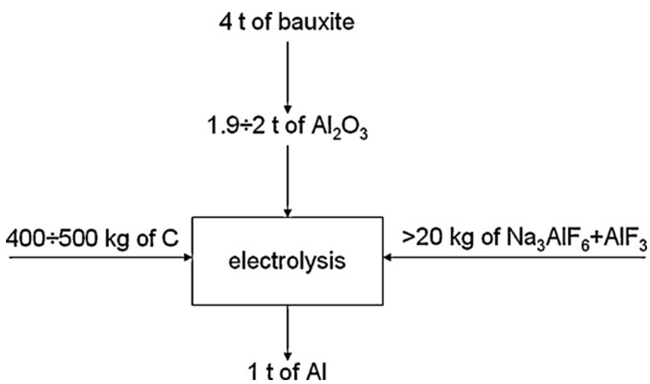

Fig. 1. Material balance for primary aluminum production.

aluminum is approximately 14 MJ, the total energy intensity of aluminum amounts to about 100 MJ/kg. The composition of aluminum energy intensity is shown in Fig. 2.

2.5. Advanced aluminum production

Aluminum industry produces metal in the form of ingots unsuitable for most aluminum applications including aluminum-based energy generation technologies.

The final energy intensity of applicable aluminum depends on further processing techniques, which can vary considerably. It is evident that to minimize the energy intensity of final product, the number and energy intensity of processing steps must be minimized as well. The initial stage of aluminum processing is usually the melting, which is intended to remelt the ingots into the shape suitable for subsequent thermomechanical processing. The melting is the most energy intense processing operation of all post-smelting processes. Theoretical energy required to bring room-temperature aluminum to 960 °C molten metal is 1.4 MJ/kg; however, due to the heat losses of furnaces the actual spending on primary aluminum remelting amounts to 9 MJ of mainly thermal energy per one kg of finally produced aluminum [69].

The purity of primary aluminum produced in Hall-Héroult process, 99.7–99.9%, is not applicable in some cases as well. Aluminum refining is carried out mostly through the three-layer electrolysis technique. The electrolytically refined purity is 99.9–99.99%. Aluminum electrolytic refining, so-called Hoopes process, requires additionally about 20 kWh/kg of only electrical energy [73] that exceeds the electrical energy of Hall-Héroult process. Due to so high energy intensity the use of high purity metal in aluminum-based energy generation technologies is, evidently, very unwanted. Further purification is achieved by zone melting, which provides the purity of 99.999–99.9999%.

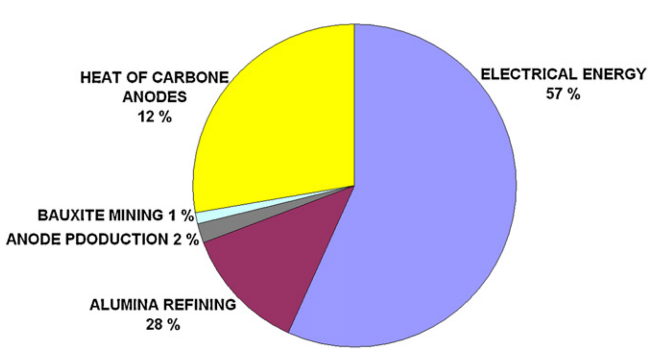

Fig. 2. Composition of aluminum energy intensity.

2.6. Cycle efficiency of aluminum-based energy storage

When aluminum is oxidized to produce the energy, aluminum oxide and/or hydroxides are formed. In general, oxidation products can be returned to the aluminum smelting process. Thus, energy required for bauxite mining and alumina refining (27.2 MJ/kg in sum) can be subtracted from total energy intensity:

$$100 - 27.2 = 72.8\,\text{MJ/kg}.$$

Calorific value of aluminum is about 31 MJ/kg. Only this energy can be usefully utilized within aluminum-fueled power plant. So, it shows the efficiency limit. If 112.8 MJ are deposited, the maximum cycle efficiency of aluminum-based energy storage is as follows:

$$\frac{31\,\text{MJ}}{72.8\,\text{MJ}} = 43\%.$$

This percentage represents the total-thermal efficiency. Electrical energy cycle efficiency depends on the efficiency of aluminum-based energy generation technology. If only electrical energy, which is consumed in aluminum smelting (56 MJ), is taken into account and the efficiency of aluminum-based energy generation technology is assumed to be 40%, the electrical energy cycle efficiency will be:

$$\frac{31 \times 0.4\,\text{MJ}}{56\,\text{MJ}} = 22\%.$$

It is clear, that the efficiency of aluminum-based energy storage is much smaller than that of any conventional energy technology. That is due to the combination of electrolytic and oxidation processes as in case of hydrogen. But, as compared with conventional transportable batteries, low cycle efficiency of aluminum is compensated by zero self-discharge and high energy density.

2.7. Perspectives of aluminum in global energy

Of course, today, in fossil fuel time, aluminum cannot be considered as the basic energy carrier instead of traditional liquid hydrocarbons. Current annual rate of primary aluminum production, about 40 million tons worldwide [56], is incomparable with global energy demands: 40 million tons of aluminum correspond to 42 million tons of coal equivalent (heat value of coal equivalent is 29 MJ/kg), while total world's energy consumption (all kinds of fuels) exceeds 10 billion tons of coal equivalent [7]. However, from bauxite resources (55–75 billion tons) it follows that the potential resource of aluminum is 14–19 billion tons or 15–20 billion tons of coal equivalent that means that, potentially, aluminum can be highly integrated into global energy.

Aluminum-based energy storage can participate as a buffer practically in any electricity generating technology. Today, aluminum electrolyzers are powered mainly by large conventional units such as coal-fired (about 40%), hydro (about 50%) and nuclear (about 5%) power plants [69,86–88]. In this field aluminum can play a role of strategic energy buffer. Due to zero self-discharge aluminum is a long term storageable and manoeuvrable fuel, which can be utilized on demand promptly. In future, if inert anodes are developed, aluminum production technology can be also integrated into distributed energy.

3. Aluminum-based energy generation technologies

Aluminum has two main oxidants: oxygen and water. In accordance with Hess's law the total heat generation in aluminum–water and hydrogen–oxygen reactions equals to heat generation in aluminum–oxygen reaction.

There are many investigations in the field of aluminum combustion in atmospheric oxygen [89–100]. They are related to

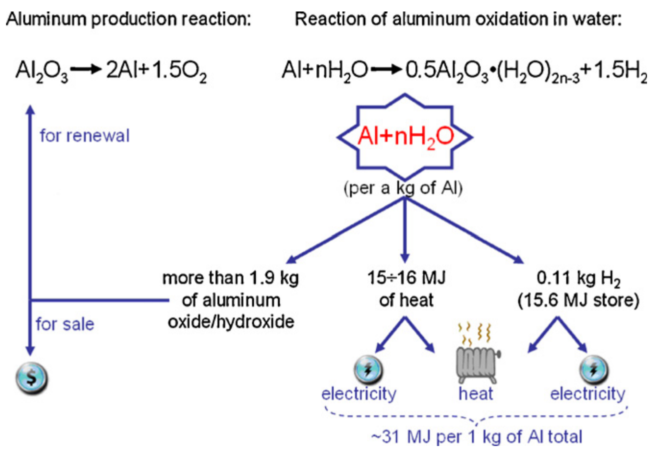

Fig. 3. Aluminum–water reaction for energy/hydrogen production.

either reaction mechanism [92–96] or reaction kinetics [97–100]. Aluminum–oxygen chemical combustion represents ungovernable high-temperature process. Therefore, the use of aluminum–oxygen combustion within non-military thermopower plant is still far from reliability. Now, this method is applied only in pyrotechnic and solid propellants [101,102].

There is another state in case of water. Due to relatively low operation temperatures, controllability and fuel cell (FC) growth, the use of water as oxidant in aluminum-based energy generation technologies attracts more attention. The energy distribution within aluminum–water reaction is shown in Fig. 3. When aluminum reacts with water, 15–16 MJ of heat, 0.111 kg of H_2 and over 1.9 kg of aluminum oxide/hydroxide are produced per a kg of aluminum. Precise heat and product composition depend on thermodynamic conditions (temperature and pressure) of aluminum–water reaction.

The energy stored in aluminum can be used in a wide spectrum of energy applications: from portable power sources to transport and stationary power plants. Each application is characterized by its own properties that influences on the technology. Generally, aluminum-based energy generation technologies can be categorized by aluminum oxidation method. First of all, these methods can be divided into two following categories:

- direct electrochemical (anodic) oxidation of aluminum;
- chemical aluminum–water reaction.

Let's review them.

3.1. Electrochemical oxidation of aluminum

The process of anodic oxidation of aluminum was opened in 1857 [103]. Since then a great number of electrochemical sources with aluminum-based anodes have been developed.

The most perspective aluminum-based battery in the view of mass usage is assumed to be aluminum–air FC battery. The oxidant in such FC is usually atmospheric oxygen. Electrolyte represents alkaline, saline or acidic aqueous solution.

The cathodic reaction of aluminum–air FC represents the oxygen reduction reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

Typical catalysts for this reaction are platinum, silver, metal nitrides such as Mn_4N, Fe_2N, CrN, manganous oxide [104,105], composite oxides with spinel [106–109] or perovskite [110,111] structure, pyrolyzed macrocycles [112–114] and activated carbon [115,116]. Oxygen reduction reaction is mainly carried out on advanced-surface electrodes, e.g. porous; active layer is generally composed of catalyst, water repelling and current conducting components.

The overall aluminum–air FC reaction can be simplified as follows:

$$4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3$$

In FC with saline electrolyte the anodic process of aluminum dissolution can be described by following equation:

$$Al \rightarrow Al^{3+} + 3e,$$

In saline electrolyte Al^{3+} is balanced by chloride ions, hydroxo and/or hydroxyl ions.

In FC with alkaline electrolyte the anodic process of aluminum dissolution leads to $Al(OH)_4^-$ formation:

$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3e \qquad (5)$$

The anodic process of aluminum dissolution is accompanied with the cathodic process of hydrogen reduction:

$$2H_2O \rightarrow H_2 + 2OH^- - 2e, \qquad (6)$$

This process known as corrosion reaction takes place on areas, where impurities such as copper, iron and silicon are localized [117,118]. It is accepted that corrosion reaction is parasitic process, which reduces the Coulombic efficiency of the anode, and must be necessarily suppressed. To minimize the corrosion reaction the anode is proposed to be produced from high-purity aluminum (with the purity not less than 99.995%) or the certain impurities must be reduced, e.g. iron [119]. However, the cost of such aluminum was estimated to be almost two times more than the cost of 99.9% purity aluminum [120]. So, it is clear, that anode based energy generation technology faces directly with the problem relating to high purity aluminum. To increase the cycle efficiency of aluminum-based energy storage, high purity aluminum must be replaced by aluminum of technical purity.

The efficiency of aluminum–air FC is increased when aluminum is alloyed with special elements such as Ga, In, Sn, Zn, Pb, Mg, Mn. It was established that such elements move the anode potential to negative field, decrease the polarization (at fixed potential current) or increase the current density (at fixed potential) of aluminum–air FC [121–138]. The improvement of anode performance by additional elements is known as activation. Activation leads to the oxide film thickness and/or composition changing or to oxide film destruction. It is achieved not only by certain composition but also by alloy preparation quality. So in [136] it was shown that alloys, which have the similar composition, can differ in electrochemical characteristics that was explained by different preparation techniques. There was also claimed that 99.98% aluminum alloy with Mg (0.6 wt.%), Sn (0.1 wt.%) and Ga (0.05 wt.%) in 2 M NaCl solution can be stable against the corrosion at room temperature for several weeks.

Activation of the anode is also achieved with the help of electrolyte additions. The influence of such additions as CaO and $CaCl_2$, sodium citrate ($Na_3C_6H_5O_7$) and stannate (Na_2SnO_3) on anode performance in 4 M alkaline solution was studied in [119,132,139,140]. All of these additions was claimed to improve the behavior of anode and allow using technical purity aluminum at optimized electrolyte composition. Technical purity aluminum was also used in [121,141], where the speed of corrosion was studied in alkaline electrolyte containing ZnO. 98.7% aluminum alloy with Mn (1.2 wt.%) and 97.5% aluminum alloy with Mg (2 wt.%) and Mn (0.25 wt.%) were found to be the suitable anode materials; 6 M ZnO was found to be the best concentration in 4 M NaOH solution. The deposition of zinc on the anode was found to strengthen in composite electrolyte with organic additions [142,143]. In [143–146]

it was proposed to use methanol as corrosion inhibitor. The speed of corrosion reaction in saline and acid electrolytes was shown to decrease also when certain ions such as Hg^{2+}, Ga^{3+}, In^{3+}, Sn^{2+}, Zn^{2+} were added into electrolyte [135,147–152].

In [42,117,153,154] the hydrogen produced during corrosion was proposed to be utilized in air–hydrogen FC. That was aimed to increase the overall electrical efficiency of a combined system and in the long run to use low grade aluminum in anode manufacturing.

Besides aluminum–air FC the aluminum as anode is used in such systems as Al–H_2O_2, Al–MnO_2, Al–AgO and Al–S. These systems apply aqueous solutions as well. Another type of electrolyte for aluminum-based anodes is molten salt. The use of molten salt is intended mainly for rechargeable technologies. Operation principle and technical characteristics of these types batteries were considered in [155].

Although theoretical energy density of generation technology based on aluminum–air FC battery is about 4300 Wh/kg and electrical efficiency is about 55% [154], the actual specific energy and efficiency are 300 Wh/kg and 45% [117,154,156] respectively.

Today, mainly lead-acid [10,11], nickel-metal hydride [14] and lithium-ion [18] batteries are planned to remove the internal combustion engines in transport sector. But, low specific characteristics, high self-discharge rate, short lifetime and high cost prevent them from scale integration into transport. The specific energy of aluminum–air FC battery has been already higher than that of transport-intended conventional accumulators, while the recharge of aluminum–air FC battery vehicle is easy as well. So, if other vital questions such as self-discharge and material cost are decided in case of aluminum–air FC battery, it can potentially compete with both internal combustion engine and other electrochemical accumulators.

3.2. Aluminum–water reaction

3.2.1. Aluminum–water reaction in alkaline solution

Hydrogen production method based on aluminum oxidation in alkaline aqueous solutions is one of the oldest and more than century-known as well [157–159]. The process of hydrogen generation in this case goes through electrochemical reactions (5) and (6). Overall reaction is described by following equation:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{7}$$

The kinetics of aluminum oxidation in alkaline aqueous solutions is a topic of many investigations, which have been continuing up to now [160–167]. Due to NaOH, KOH, $Ca(OH)_2$ comparison [165] it was established that NaOH is the best hydroxide for aluminum alloys oxidation in the view of reaction rate and conversion degree. To reach the same reaction rates in case of KOH the higher alkali concentration or temperature as compared with NaOH are required [164]. Kinetics of aluminum oxidation in NaOH solution depending on molar ratio NaOH/Al was studied in [160,162,167]. From those works it can be concluded that optimal conditions for this reaction are 70–90 °C and 5.75 M NaOH solution. Hydrogen yield and reaction rate increase when sodium aluminate ($NaAlO_2$) solution instead of NaOH is used at the same pH level [163]. In [168] aluminum oxidation in $NaAlO_2$ solution with $Al(OH)_3$ additions was studied. It was established that $Al(OH)_3$ prevents the oxide film growing on the surface of aluminum particles that in the long run accelerates the chemical reaction. 0.01 M $NaAlO_2$ + 20 g/dm^3 $Al(OH)_3$ were chosen as optimum (pH = 12); maximum hydrogen generation rate was 200 cm^3/min per a gram of aluminum. Oxidation kinetics of different aluminum-based alloys in alkaline aqueous solutions was studied in [165,169]; it was determined that Al–Si alloys have the most oxidation rate and conversion degree. In [166] it is claimed that the mixture of aluminum (its alloys) and sodium borohydride ($NaBH_4$) is the perspective matter for hydrogen generation, because the hydrolysis of $NaBH_4$ increases the pH of aqueous solution while aluminum alloys have a catalytic influence on the hydrolysis process.

The reaction of aluminum oxidation in alkaline solutions has been already applied in a great number of hydrogen generators [157,158,160,161,170–178] and energotechnological plants [161,179,180].

The design of co-generation energotechnological plant based on aluminum oxidation in alkaline solution, was described in [161]. In [177] it was shown that the hydrogen produced during aluminum waste cans oxidation in 2 M NaOH aqueous solution can be successfully utilized in air–hydrogen FC. FC in that case showed better electrical characteristics than in case when it was fed by hydrogen from proton exchangeable membrane electrolyzer. Hydrogen generators combined with air–hydrogen micro-FC was shown to suit for portable power sources [178].

The efficient recycling of waste aluminum was proposed in [161,180]. Aluminum is utilized within the special reactors filled with NaOH solution at high pressures (up to 30 MPa) and relatively moderate temperatures (to 150 °C) to produce high-purity compressed hydrogen and marketable aluminum hydroxide. Aluminum hydroxide is supposed to return to aluminum metallurgy or go into market of inorganic materials (Fig. 3). Possible design and operation principle of such reactors are shown in [181]. High thermodynamic (up to 90%) and economic efficiencies of such co-generation approach proved in exergetic life cycle assessment [179].

Aluminum-fueled adsorption refrigeration plant was proposed in [182]. In that plant the scrap aluminum as fuel and alkaline aqueous solution as oxidant were used for hydrogen production. Hydrogen was then chemically combusted to produce the heat, which is then utilized within ammonia–water cycle: increase the speed of separation of ammonia from water.

Main advantages of aluminum oxidation in alkaline solution are simplicity and relatively low cost of necessary reagents and equipment. The technologies, which are based on this oxidation method, can be applied in portable field, transport and stationary. But, probably the single and at the same time the essential disadvantage of this method is high corrosiveness of working medium.

3.2.2. Mechanochemical activation of aluminum

This type of aluminum activation supposes to use additional chemical substances whose physicochemical properties influence on aluminum reactivity.

One of the oldest methods of chemical activation of aluminum is amalgamation [183,184]. 3–5 wt.% hydrargyrum addition increases the hydrogen production rate up to 1440 cm^3/min per a gram of aluminum [185]. However, the toxicity of this approach prevents it from practice.

The activity of aluminum in water increases by alloying with different metals such as Ga, In, Re, Bi, Mg, Ca [186–192]. The additions act specifically on mechanical strength of cast solid due to adsorptive penetration, so-called Rebinder effect [193]. Such activation allows carrying out the aluminum–water reaction at relatively moderate temperatures. Multi-element aluminum-based alloys doped with Zn, Sn, Ga and In were studied in [190,191]. Although the alloys showed an appropriate oxidability with 96% conversion degree after 0.5 h, the cast solid suffered from the necessity of its cryogenic storage (at liquid nitrogen temperatures) [190]. This problem is solved by mechanochemical activation of aluminum [186,192]. After this activation the reagent can be stored under room temperatures. The reaction time of mechanochemically activated aluminum is several minutes, while the conversion degree nears to theoretical value.

Another mechanochemical activation of aluminum is NaCl doping [194–197]. The study of microstructure, specific surface area

and chemistry of aluminum powder doped with NaCl is presented in [194]. In [196] it was established that optimal NaCl to Al mass ratio is 2; average speed of hydrogen generation increases from 100 to 200 cm^3/min per a gram of aluminum with temperature increasing from 55 °C to 70 °C.

Mechanochemical activation of aluminum was proposed to be used in special cartridges to produce hydrogen for portable air–hydrogen FC [197–200]. Some prototypes of aluminum-based portable power sources with air–hydrogen FC have been already made [198–200].

3.2.3. Mechanical activation of aluminum

Aluminum can react with water and produce hydrogen also due to mechanical activation [98,201,202]. It implies no chemical additions and can be divided into in-process activation and pre-activation.

The concept of in-process activation is described in [201,202]. Activation process and aluminum oxidation occurs simultaneously. Activation may represent cutting, grinding or other. It implies that fresh uncovered by oxide film surface of aluminum, which is produced during activation, immediately falls into oxidative medium. During in-process activation the aluminum is oxidized due to pitting corrosion. The use of wet cutting of aluminum alloys was proposed for hydrogen generation in [201].

By preliminary mechanical activation here, the production of ultra dispersed aluminum powder is implied. This activation represents the stand-alone processing characterized by high energy consumption. Ultrafine aluminum powder is produced today generally by electrical explosion of aluminum wire [203–206], plasma-based atomization [207–209], inductive method [210], aluminum reduction from its halides in alkali steam [211–213] and decomposition of metalorganic compounds [214–216].

Industrially produced aluminum powders are shown to be unsuitable for aluminum–water reaction at relatively moderate temperatures [217,218]. The conversion degree of aluminum micron powder in pure, without any activation additions, water at temperatures below 100 °C is far from 100%. After 5 h staying within special 100 °C water-filled reactor under intensive mixing the conversion of aluminum powder with average particle size of 20 μm was less than 60% [217].

On the contrary, nano-sized aluminum powder reacts with pure, without any activation additions, water with high reaction rate and conversion degree [99,100]. The conversion of aluminum powder with average particle size of 140 nm in water at 50–70 °C was close to 1; the reaction time decreased from 40 min for 50 °C to 20 min for 70 °C [99].

Due to its high chemical activity, the ultrafine aluminum powder has been already proved to be an appropriate material for pyrotechnic compositions and solid propellants [101,102]. But, its use for electrical, thermal or kinetic energy production is connected with a number of drawbacks caused by the same high activity of nanoscale powders. Following the explosion characteristics comparison between aluminum micron and submicron powders it was established that the last one has bigger maximum explosion pressure, bigger maximum rate of pressure rise and smaller minimum ignition energy [219]. Ultrafine powder must be kept under inert atmosphere or special passivating films should be created on particles surface when powder is produced [220–222]. Moreover, when aluminum powder dispersity increases, the percentage of active metal and the apparent density of powder decrease [98].

Chemical and (or) mechanical activation of aluminum results in considerable rise in reagent cost. The cost of activated aluminum is increased by both the use of expensive rare metals and high power consumption. Therefore, it is evident that the preliminary activated aluminum cannot compete with oil and the field of its application is only portable. From available 31 MJ/kg of stored in aluminum energy, maximum half can be really converted into electrical energy, because the effective utilization of heat of aluminum–water reaction in portable scale is practically impossible. Useable heat represents the chemical energy of produced hydrogen (Fig. 3) and it is converted into electrical energy with the efficiency of FC. If FC efficiency is 50%, a kg of aluminum returns about 7.5 MJ of electrical energy (about 25% from available energy stored in aluminum). So, if the stoichiometric water is taken into account, the theoretical energy density of the system based on activated aluminum is about 2.5 MJ/kg (700 Wh/kg). If water, which is produced in air–hydrogen FC, is supposed to return from FC to aluminum–water reaction, the energy density will be increased to 3.75 MJ/kg (1040 Wh/kg) that considerably exceeds energy densities of conventional batteries.

3.2.4. High-temperature aluminum–water reaction

Aluminum–water reaction can be initiated by high temperatures. Due to high temperatures the aluminum can be used in the form of micron powders, which are produced from the melt by standard pulverization method [223]. So, the production of micron powder needs less energy than ultrafine powder production.

Mechanism and kinetics of high-temperature aluminum–water reaction were studied recently within the combustion theory [92–100,224–227]. It was established that aluminum combustion in water differs considerably from combustion in air. In [100] spherical aluminum particles with average size of 3–4.5 μm when linearly heated (at rates of 1–20 °C/min) in waterlogged air were totally oxidized before 1000 °C while in dry oxygen the reaction finished at 1500 °C.

Aluminum–water reaction at stoichiometric mass ratio goes, theoretically, under about 3000 °C. High-temperature hydrogen produced was proposed to be used in magnetohydrodynamic generator [228,229]. However, although this method promises high thermodynamic efficiency (about 40%), for date it has been only theoretically evaluated and doesn't have practical realization.

Kinetics of aluminum oxidation in wet steam of water at temperatures before 250 °C was studied in [230]. Reaction time and conversion degree of aluminum powder with average particle size of 24 μm were explored depending on steam temperature. Maximum conversion degree was found to be 80%, while the reaction lasted several hours.

Oxidation kinetics of aluminum micron powder in boiling water at temperatures 230–370 °C was studied depending on powder size and temperature in [231]. It was established that aluminum powder with average particle size up to 70 μm is intensively oxidized in boiling water at temperature over 230 °C, the conversion degree is close to 100% and the reaction lasts only several tens of seconds. That method laid the basis for the technology of hydrogen, heat and aluminum oxide/hydroxide co-production [232–234]. An experimental power plant created had 12% electrical efficiency and about 70% total efficiency [235].

Thermodynamic efficiency of aluminum–water reactors as steam–hydrogen generators was studied in [181,236–239]. Theoretical investigations showed both high electrical efficiency (up to 40–45%) and high total efficiency (60–80%).

Aluminum micron powder oxidation in seawater was proposed for the creation of submarine propulsion system [240]. It is based on aluminum–water reactor and steam–hydrogen turbine. Steam–hydrogen mixture produced within the reactor speeds up the turbine. Temperature and pressure of steam–hydrogen mixture before turbine are 800–1000 °C and 2–5 MPa respectively. Although the propulsion system is just theoretically developed, some of its components have been already tested.

Co-generation power plant based on high-temperatures aluminum oxidation in water steam was modeled in [241]. High-pressure steam–hydrogen mixture goes from the reactor into

Table 5
Summary of aluminum-based energy generation technologies.

Oxidation method	Application areas	Electrical efficiency (related to aluminum calorific value), %	Energy density, Wh/kg	Priority problems
Electrochemical oxidation of aluminum	Portable, Transport, Stationary	55	4300	High purity aluminum
Aluminum–water reaction in alkaline solution	Portable, Transport	25	1040	Designing
	Stationary	45	8600	
Mechanochemical activation of aluminum	Portable	25	1040	Use of rare metals, High energy intensity
Mechanical activation of aluminum	Portable	25	1040	High energy intensity
High-temperature aluminum–water reaction	Stationary	45	8600	Designing

the turbine and then from the turbine into the heat exchanger. Power plant is evaluated to produce 80 kW of electrical and 130 kW of thermal energy. Theoretical power plant total efficiency is 40%.

Due to relatively high temperatures, main applicable fields for this technology are stationary and probably transport. If water is supposed to be present on site where energy is produced, the energy density of aluminum-based energy storage will be equal to that of aluminum (8600 Wh/kg), because in this case only the metal needs to be stored and transported. High temperature of reaction products, in particular steam–hydrogen mixture, provides high thermodynamic efficiency of aluminum-based energy generation. The use of industrial powders is an efficient aluminum-based energy storage technology, because energy intensity of these powders is most close to energy intensity of primary aluminum.

3.3. Oxidation methods summary

The summary of aluminum-based energy generation technologies is presented in Table 5.

4. Conclusion

Main conclusions, which can be marked from this work, are as follows:

1. Global energy is ever-changing organism. Today, as never before, this organism needs to store the at all scales: from portable and transport to large stationary. Energy storage technologies are required to remove the oil from transport, to support the renewable, distributed and Smart-grid energy and to smooth the load of conventional power plants.
2. Although there are a great number of commercially available energy storage technologies, none of them can be referred to as universal and each has its own specialized application areas. Moreover, there are no appropriate transportable energy storage technologies, which might compete with oil in its traditional niches (transport and small stationary).
3. Hydrogen is proposed to be used as energy storage and carrier. But, storage and transportation of hydrogen are still open problems, as several decades ago.
4. In this work aluminum was considered as energy storage and carrier. To produce 1 kg of aluminum, 2 kg of alumina, 0.4–0.5 kg of coal, 0.02–0.08 kg of cryolite and 13.4–20 kWh of electrical energy are required. Total energy intensity of aluminum was estimated to be about 100 MJ/kg. Cycle efficiency of aluminum-based energy storage does not exceed 43%.
5. Although aluminum production is very energy intensive process with high greenhouse gas emissions, some physical–chemical properties of aluminum are very attractive for energy storage and carrying. Among them there are zero self-discharge and high energy density. Aluminum can be stored for a long time and transported to any distance.
6. There are a number of aluminum-based energy generation technologies. Different technologies are based on different aluminum oxidation methods and intended for different application areas.
7. For portable applications the most appropriate solutions are electrochemical oxidation of aluminum, aluminum–water reaction in alkaline solution and oxidation of activated (mechanochemically or mechanically) aluminum. Direct electrochemical oxidation has, theoretically, 4300 Wh/kg energy density and about 55% electrical efficiency. Technologies based on chemical aluminum oxidation can reach 1040 Wh/kg energy density and 25% electrical efficiency. Electrochemical oxidation of aluminum and aluminum–water reaction in alkaline solution suit also for transport.
8. Stationary is for high-temperature aluminum–water reaction and aluminum–water reaction in alkaline solution. Theoretical electrical efficiency is about 45%, while energy density equals to its maximum value, 8600 Wh/kg, because transportation to stationary power plant is assumed to be required only for aluminum.
9. Today, aluminum cannot be considered as the basic energy carrier instead of traditional liquid hydrocarbons. It might be highly integrated into global energy in post-fossil fuel era. But, there are a number of special aluminum-based applications already for today. The coming of aluminum-based energy storage technologies is expected in some portable applications and small-power eco-cars. Since energy generation based on aluminum is cleaner than that of fossil fuel, the use of aluminum is defensible within polluted areas, e.g. within megapolises. Aluminum can be applied also in remote non-electrified areas, disaster areas, within ground and underground systems of defense infrastructure and within power systems of ships including submarines. Another today's perspective application is hydrogen and aluminum oxide/hydroxide co-production technology.

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